



Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number: **0 482 783 A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 91309159.1

(51) Int. Cl.⁵: H01M 8/12, H01M 8/24

(22) Date of filing: 07.10.91

(30) Priority: 24.10.90 GB 9023091

(43) Date of publication of application:
29.04.92 Bulletin 92/18

(84) Designated Contracting States:
BE DE FR GB IT NL

(71) Applicant: **IMPERIAL CHEMICAL INDUSTRIES PLC**
Imperial Chemical House, Millbank
London SW1P 3JF(GB)

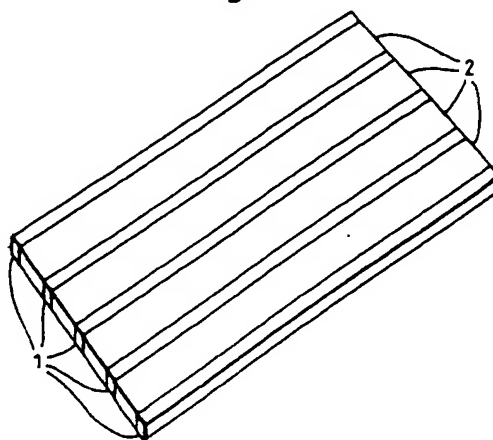
(72) Inventor: **Kendall, Kevin**
7, Whiteley Close
Runcorn Cheshire(GB)

(74) Representative: **Walmsley, David Arthur Gregson et al**
Imperial Chemical Industries PLC Legal
department: Patents PO Box 6 Bessemer
Road
Welwyn Garden City Hertfordshire AL7
1HD(GB)

(54) **Composite membranes and electrochemical cells containing them.**

(57) A composite membrane comprising one or more domains of an electrolyte material and one or more domains of an electronically conducting interconnect material, said electrolyte domain(s) and said interconnect domain(s) traversing the thickness of the membrane so that the membrane comprises contact surfaces for the or each electrolyte domain and the or each interconnect domain on both major faces thereof. Also claimed is an electrochemical cell comprising the composite membrane and having one or more anodes arranged on one major face and one or more cathodes arranged on the other major face of the membrane.

Fig.1.



EP 0 482 783 A2

thodic electrode material on the opposing major face thereof. The width of each anode band will be such that it overlaps an interconnect striation and the electrolyte band on one or both sides thereof. The width of the cathodic electrode bands will also be similarly governed. The electrode bands may be continuous or discontinuous, but are preferably continuous.

Suitable materials for the fabrication of the electrolyte/interconnect membrane and the electrode components are the solid inorganic materials which possess the requisite properties to function as an electrolyte, an interconnect or an electrode. Such materials include, inter alia, metals, metal alloys, ceramics and ceramic/metallic materials (cermets). Ceramics and cermets are especially preferred materials for the fabrication of the membranes and electrochemical cells of the invention. Preferably, the thermal expansion coefficients of the components of the electrochemical cell do not differ by more than 10 %, so as to reduce the risk of delamination or cracking when the cell is in use.

The composite membranes of the invention are conveniently fabricated from particulate electrolyte and interconnect materials which can be formed into an integral mass by sintering, i.e. by the application of heat and, optionally, pressure. The particulate electrolyte and interconnect materials can be separately agglomerated into sinterable masses by dispersion in a binder comprising an organic polymer in solution or dispersion in a liquid vehicle, so as to form a coherent, dough-like composition having sufficient deformability to allow for the shaping thereof. Polymer doughs separately containing the particulate electrolyte material and the particulate interconnect material can be shaped and assembled into a dough layer which is then formed into a thin cohesive sheet (precursor membrane), e.g. by rolling, pressing or extrusion. The precursor membrane comprises one or more domains of the particulate electrolyte material and one or more domains of the particulate interconnect material bound together by the polymeric binder. The liquid vehicle can be actively or passively removed from the precursor membrane by evaporation and the polymer burned-out prior to effecting sintering of the particulate masses to form the composite membrane. It will be appreciated that the dough layer may comprise many separate pieces of suitably shaped dough material comprising respectively particles of electrolyte material and particles of interconnect material.

For example, to form a composite membrane having an alternating arrangement of essentially parallel interconnect striations and electrolyte bands, strips of a deformable dough comprising dispersed particles of an electrolyte material can be laid up between strips of a deformable dough

comprising dispersed particles of an interconnect material, to form a dough layer comprising alternating strips of the two dough materials. The strips of dough may be produced directly by a rolling, pressing or extrusion processes or they may be cut from a moulded sheet of the dough which has been produced using such processes. At this stage the dough layer may be pressed from the sides to loosely knit the strips together. The dough layer can then be rolled, pressed or otherwise moulded to unite the strips into a thin cohesive sheet which constitutes the precursor membrane. The so formed precursor membrane can then be treated as described above to form the composite membrane.

The fabrication of a composite membrane using the above described techniques is particularly desirable, since the polymer containing precursor membrane tends to possess a degree of inherent flexibility which allows it to be wrapped around formers, e.g. fibrous ceramic boards, to produce non-planar shapes, for example a corrugated shape, a spiral or a tube. The burning-out and sintering operations tend to fix the composite membrane in the required shape, allowing for removal of the formers, if desired. This property allows a large area of the composite membrane to be stored in a compact space, so that apparatus comprising the membrane can be made less cumbersome. Of course, we do not exclude the possibility that the composite membrane itself may possess sufficient flexibility to enable it to be arranged into a corrugated, spiral or other non-planar shape.

Alternatively, polymer doughs separately containing the particulate electrolyte and particulate interconnect materials can be shaped and assembled into a block, e.g. a cylindrical block, which is then extruded through a die to yield a tubular precursor membrane comprising one or more domains of particulate electrolyte material and one or more domains of particulate interconnect material bound together by the polymeric binder. Removal of the liquid medium, burning out of the polymer and sintering yields a tubular shaped composite membrane. Extrusion techniques for making tubes are known in the art and can be applied to the manufacture of tubular composite membranes.

A preferred tubular composite membrane comprises one or more bands of electrolyte material and one or more striations or stripes of interconnect material which are contiguous with one another and extend along the length of the tube from one end thereof to the other. A tubular membrane of this type can be prepared by extrusion of a cylindrical block constructed from the interconnect and electrolyte containing polymer doughs by arranging the interconnect polymer dough in one or more segments which run along the length of the

and interconnect striations, bearing in mind that a given electrode should contact both an interconnect striation and an electrolyte band.

Where the electrochemical cell is fabricated from a precursor cell, it is preferred that the burning out and sintering shrinkage of the various components of the precursor cell should not differ by more than 5 %. Differences in shrinkage of greater than 5 % may lead to delamination and cracking during the burning-out and/or sintering operations.

In use, the electrochemical cell will be provided with terminal connectors which transfer current to or collect current from the electrodes. Suitable materials for the formation of the terminal connectors are the materials having good conductivity (i.e. low resistivity) such as metals, metal alloys and cermets. Especially preferred materials are the cermets due to their resistance to reactive chemical environments and high temperatures.

The electrochemical cell of the invention is particularly suitable for use in SOFC assemblies. SOFC's are electrochemical systems that convert the chemical energy of the reactants into electrical energy. The SOFC operates at approximately 1000 °C, burning fuel at the anode and consuming an oxidant at the cathode. In a SOFC assembly a gaseous fuel, e.g. hydrogen or a hydrocarbon such as methane, is caused to flow over the anode face of the electrochemical cell, and an oxidant gas, which is usually oxygen, but may be air, is caused to flow over the cathode face of the electrochemical cell. Mobile O^{2-} ions travel across the electrolyte from the cathode (air electrode) to the anode (fuel electrode) and arrive at the electrolyte/anode interface where they react with the gaseous fuel within the porous anode.

When the electrochemical cell is to be used in a SOFC assembly, the electrolyte should be impervious to the fuel and oxidant gases and should be chemically resistant to those gases, and the reactive environment which prevails, during operation of the SOFC. The electrolyte should also be conductive to O^{2-} ions. Suitable materials for the electrolyte may be selected from the inorganic oxides, in particular the ceramic oxides such as hafnia (HfO_2), yttria (Y_2O_3), zirconia (ZrO_2) and yttria, ceria or rare earth stabilised zirconia, the latter materials optionally including a proportion of indium oxide (In_2O_3) or praseodymia (Pr_2O_3). Particularly preferred materials are zirconia and especially yttria stabilised zirconia. A preferred electrolyte has a density which is at least 90 %, e.g. 95%, of the theoretical density of the material of which it is composed, and a closed porosity amounting to less than 10 volume %, e.g. 5 volume %.

When the electrochemical cell is to be used in a SOFC assembly, the interconnect should be impervious to the fuel and oxidant gases and should be chemically resistant to those gases, and the reactive environment which prevails, during operation of the SOFC. The interconnect should also be an electronic conductor. Suitable materials for the interconnect may be selected from the perovskite ceramics having the general formula ABO_3 , where A is, for example, La or Pb and B is, for example, Cr, Co, Zr or Ti, optionally doped with alkaline earth metals such as Sr, Mg or Ca. Another suitable material for the interconnect may be Nb doped titanium glass composite. Preferred materials for the interconnect are lanthanum cobaltite ($LaCoO_3$), lanthanum chromite ($LaCrO_3$) and especially alkaline earth metal doped lanthanum chromite. A preferred interconnect has a density which is at least 90%, e.g. 95%, of the theoretical density of the material of which it is composed, and a closed porosity amounting to less than 10 volume %, e.g. 5 volume %.

When the electrochemical cell is to be used in a SOFC assembly, the anode or fuel electrode should be stable to the fuel, and the reactive environment which prevails, during operation of the SOFC. Suitable materials for the anode may be selected from the porous metals such as Ni, and especially the porous cermets, particularly cermets of Ni and an inert phase such as zirconia or yttria stabilised zirconia. Other suitable anode materials may be selected from $PrInO_3$, $Hf_2In_2O_7$ or a solid solution of indium oxide (In_2O_3) containing hafnia, praseodymium dioxide (PrO_2) or $PrO_{1.83}$. Preferred materials are zirconia nickel cermets and yttria stabilised zirconia nickel cermets, especially the latter. The nickel may be added as nickel oxide which is reduced to the metal in the reducing fuel atmosphere as the SOFC is heated. A preferred anode has a density which is less than 80%, e.g. 70%, of the theoretical density of the material of which it is composed, and an open porosity amounting to more than 20 volume %, e.g. 30 volume %.

When the electrochemical cell is to be used in a SOFC assembly, the cathode or air electrode should be resistant to oxidation by the oxidant gas (air or oxygen), and the reactive environment which prevails, during operation of the SOFC. The cathode must permit rapid diffusion of the air or oxygen to the electrolyte/anode interface. A suitable material for the cathode is a Sr doped lanthanum manganite perovskite. A preferred cathode has a density which is less than 80%, e.g. 70%, of the theoretical density of the material of which it is composed, and an open porosity amounting to more than 20 volume %, e.g. 30 volume %.

vinyl butyral and cyclohexanone in weight proportions 100/6/9 using a twin roll mill, to form a deformable electrolyte dough which was de-aired by pressing into a 1 mm thick sheet using 5 MPa pressure. This sheet was cut into strips 10 mm wide and the strips were assembled into an alternating electrolyte/interconnect dough layer with similarly prepared, 1 mm wide, dough strips of interconnect material. The interconnect material was Sr doped lanthanum chromite powder. Dough strips 10 mm wide and 0.3 mm thick comprising either particulate zirconia nickel cermet (i.e. the anodic electrode material) or Sr doped lanthanum manganite powder (i.e. the cathodic electrode material) were prepared in the same way as described above. The anode dough strips were laid down on one face of the electrolyte/interconnect dough layer and the cathode dough strips were laid down on the opposing face. The resulting dough tri-layer was pressed and then calendered on a roll mill to form a precursor cell in the form of a thin tape of 0.2 mm thickness. This tape was wrapped around zirconia fibre boards to form a convoluted structure which was then heated to 90 °C to evaporate the solvent. The polymer binder was burned out by increasing the temperature at 1 °C/minute to 550 °C, and the resulting particulate assembly sintered at 1500 °C for 1 hour. The fibre boards were removed and the electrochemical cell retained the shape shown in Figure 3.

Example 2

This Example illustrates the preparation of a tubular composite membrane and electrochemical cell.

Zirconia powder stabilised with 8 mol% yttria (HSY8 Daichi Kigenso; modified to sinter at 1500 °C) (the electrolyte material) was mixed with polyvinyl butyral and cyclohexanone in weight proportions 60/5/7 using a twin roll mill, to form a deformable electrolyte dough which was de-aired by pressing into a 1 mm thick sheet using 5 MPa pressure. This sheet was cut into circular discs 13 mm in diameter, and a 40° segment of material was removed from each disc. The discs of electrolyte dough were then stacked in coaxial relation with the removed segments in line to form a rod shaped stack having a longitudinally extending open segment. An interconnect dough containing Ca doped lanthanum chromite powder (the interconnect material), polyvinyl butyral and cyclohexanone in weight proportions 60/5/7 was prepared on a twin roll mill. The interconnect dough was filled into the open segment to form a cylindrical rod which was then loaded into a ram extruder and

extruded to give a tubular precursor membrane having an outer diameter of 2.5 mm and a wall thickness of 250 µm.

The tube was then dried, heated at 1 °C/minute to 500 °C in order to burn out the polymer binder and finally heated at 1500 °C for 1 hour to sinter the particulate electrolyte and interconnect materials. The resulting tubular composite membrane was mainly composed of electrolyte material and comprised a 1 mm wide stripe of interconnect material which extended along the length of the tube. The tube had the form shown in Figure 4.

Electrode components were then applied to the inner and outer surfaces of the tubular composite membrane by coating. A first coating composition prepared by dispersing lanthanum strontium manganite powder (a cathodic electrode material) in a polymer/solvent (cellulose/terpineol) liquid vehicle was poured down the inside of the tubular composite membrane. Any excess of the coating composition was drained away to leave a coating of the particulate cathode material on the inner surface of the tube. A second coating composition prepared by dispersing nickel oxide and stabilised zirconia powder (an anodic electrode material) in a polymer/solvent (cellulose/terpineol) liquid vehicle was painted on the outer surface of the tube in the region of the electrolyte domain, care being taken to avoid the interconnect stripe. The coated tube was allowed to dry and then heated at 1 °C/minute to 500 °C in order to burn out the cellulose polymer. Finally, the coated tube was fired at 1200 °C to sinter the electrodes.

A plurality of electrode coated tubes prepared as described above can be assembled in juxtaposition to form an electrochemical cell in which the exposed surface of the interconnect stripe of one composite membrane (i.e. the surface which was not coated with the anode) contacts an anode coated on the outer surface of an adjacent composite membrane. In such an electrochemical cell, the interconnect stripe of a given composite membrane makes contact with the cathode coated on the inner surface of that membrane and an anode coated on the outer surface of an adjacent membrane.

Example 3

This Example illustrates the preparation of a tubular composite membrane.

Zirconia powder stabilised with 8 mol% yttria (HSY8 Daichi Kigenso; modified to sinter at 1500 °C) (the electrolyte material) was mixed with polyvinyl butyral and cyclohexanone in weight proportions 60/5/7 using a twin roll mill, to form a deformable electrolyte dough which was de-aired by

5. A composite membrane as claimed in claim 1 or claim 2 characterised in that it has a tubular shape.
6. A composite membrane as claimed in claim 5 characterised in that it comprises one or more bands of electrolyte material and one or more striations of interconnect material which extend along the length of the tube.
7. An electrochemical cell comprising:
 - (a) at least one composite membrane having one or more domains of an electrolyte material and one or more domains of an electronically conducting interconnect material, which domains traverse the thickness of the membrane;
 - (b) one or more anodes arranged on one major face of the or each composite membrane; and
 - (c) one or more cathodes arranged on the other major face of the or each composite membrane.

the arrangement of the components in the cell being such that the or each electrolyte domain and the or each interconnect domain make contact with both an anode and a cathode, and the or each anode and the or each cathode make contact with both an electrolyte domain and an interconnect domain.
8. An electrochemical cell as claimed in claim 7 characterised in that it comprises:
 - (a) a composite membrane(s) having a plurality of domains formed from the electrolyte material and a plurality of domains formed from the interconnect material;
 - (b) a plurality of anodes arranged on one major face of the membrane(s); and
 - (c) a plurality of cathodes arranged on the other major face of the membrane(s).
9. An electrochemical cell as claimed in claim 8 characterised in that it comprises:
 - (a) a composite membrane(s) comprising an alternating arrangement of electrolyte bands and interconnect striations which extend between the opposing edges of the membrane;
 - (b) a plurality of anode bands arranged on one major face of the membrane(s); and
 - (c) a plurality of cathode bands arranged on the other major face of the membrane(s).
10. An electrochemical cell as claimed in any one of claims 7 to 9 characterised in that it has a corrugated or spiral shape.
11. An electrochemical cell as claimed in claim 7 or claim 8 characterised in that it comprises:
 - (a) a tubular composite membrane(s);
 - (b) one or more anodes arranged on one of either the inner or outer surface of the tubular composite membrane(s); and
 - (c) one or more cathodes arranged on the other of either the inner or outer surface of the tubular composite membrane(s).
12. An electrochemical cell as claimed in claim 11 characterised in that the composite membrane(s) comprises one or more bands of electrolyte material and one or more striations of interconnect material which extend along the length of the tube.
13. A solid oxide fuel cell comprising one or more of the composite membranes claimed in any one of claims 1 to 6.
14. A solid oxide fuel cell comprising one or more of the electrochemical cells claimed in any one of claims 7 to 12.
15. A method of preparing a composite membrane as claimed in any one of claims 1 to 6 which method comprises the steps of:
 - (1) separately dispersing a particulate electrolyte material and a particulate interconnect material in a polymer based binder to form mouldable electrolyte and interconnect doughs;
 - (2) forming the electrolyte and interconnect doughs into a cohesive precursor membrane comprising one or more domains of the particulate electrolyte material and one or more domains of the particulate interconnect material each bound together by the polymer based binder;
 - (3) removing the polymer based binder; and
 - (4) sintering the particulate electrolyte and interconnect materials to form the composite membrane.

Fig. 3.

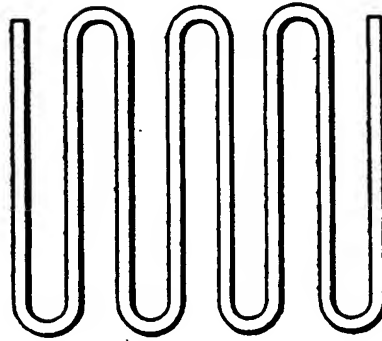
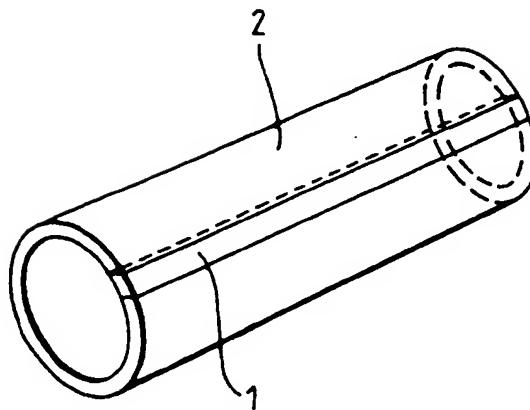


Fig. 4.



(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 482 783 A3

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 91309159.1

(51) Int. Cl.⁵: **H01M 8/12, H01M 8/24,
C04B 35/00**

(22) Date of filing: 07.10.91

(30) Priority: 24.10.90 GB 9023091

(43) Date of publication of application:
29.04.92 Bulletin 92/18

(64) Designated Contracting States:
BE DE FR GB IT NL

(66) Date of deferred publication of the search report:
14.04.93 Bulletin 93/15

(71) Applicant: **IMPERIAL CHEMICAL INDUSTRIES
PLC**
Imperial Chemical House, Millbank
London SW1P 3JF(GB)

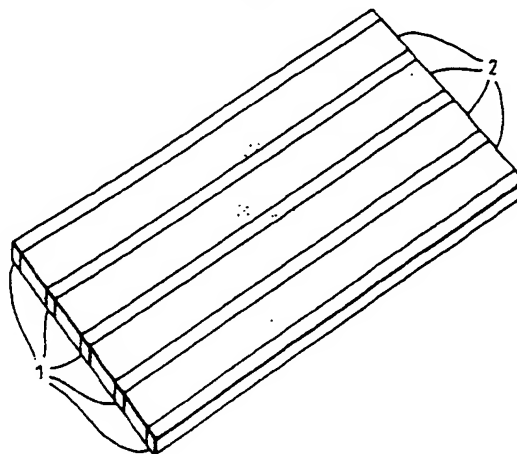
(72) Inventor: **Kendall, Kevin**
7, Whiteley Close
Runcorn Cheshire(GB)

(74) Representative: **Walmsley, David Arthur
Gregson et al**
ICI Group Patents Services Dept. PO Box 6
Shire Park Bessemer Road
Welwyn Garden City, Herts, AL7 1HD (GB)

(54) **Composite membranes and electrochemical cells containing them.**

(57) A composite membrane comprising one or more domains of an electrolyte material (2) and one or more domains of an electronically conducting interconnect material (1), said electrolyte domain(s) and said interconnect domain(s) traversing the thickness of the membrane so that the membrane comprises contact surfaces for the or each electrolyte domain and the or each interconnect domain on both major faces thereof. Also claimed is an electrochemical cell comprising the composite membrane and having one or more anodes arranged on one major face and one or more cathodes arranged on the other major face of the membrane.

Fig.1.



EP 0 482 783 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 9159

Page 2

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	PATENT ABSTRACTS OF JAPAN vol. 05, no. 146 (P-080)16 September 1981 & JP-A-56 079 951 (NGK SPARK PLUG CO LTD) 30 June 1981 * abstract *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 FEBRUARY 1993	Examiner D'HONDT J.W.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EP FORM 180 (01.91) (P0001)